Luminescence of CsPbCl₃ nanocrystals dispersed in a CsCl crystal under high-energy excitation

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A CsPbCl₃ single crystal is characterized by an intense luminescence of free excitons with the main decay time $\tau \leq 0.5$ ns. It has been considered as a perspective material for fast scintillators. Owing to that, CsPbCl₃ nanocrystals are of great interest in view of the search of materials suitable for the registration of high-energy radiation in the nanosecond time interval.

The study of the luminescence decay kinetics of CsPbCl₃ nanocrystals dispersed in a CsCl matrix is necessary for the clarification of the mechanism of high-energy radiation transformation into intrinsic electronic excitations of CsCl matrix and CsPbCl₃ nanocrystals. From the practical point of view, such investigations allow to establish the possibility of application of these materials for the registration and visualization of high-energy radiation.

The single crystal of CsCl:Pb was grown by the Stockbarger method from zone-refined CsCl salt containing 0.5 mol % of PbCl₂ in the melt. To produce the CsPbCl₃ nanocrystals dispersed in a CsCl matrix, the CsCl:Pb crystal was annealed for 20 hours at 200 °C after its fast quenching down from 450 °C. Such thermal treatment results in a partial transformation of the Pb²⁺ centres, existing in a quenched CsCl:Pb crystal, into CsPbCl₃ nanocrystals of a fixed size. As not all the Pb²⁺ centres were thermally transformed into CsPbCl₃ nanocrystals, both Pb²⁺ centres and CsPbCl₃ nanocrystals were observed in the CsCl:Pb crystal studied.

The time-resolved spectroscopy method was used for the study of the luminescence characteristics. The experiments were carried out at SUPERLUMI station in HASYLAB (Hamburg, Germany).

The luminescence spectrum of the annealed CsCl:Pb crystal excited at 10 K in the transparency region of a CsCl:Pb crystal ($E_{\text{exc}}=5.12$ eV, i.e., 242 nm) consists of the narrow band peaking at $E_{\text{em}}=2.98$ eV (416 nm) which is similar to the free exciton emission band of a CsPbCl₃ single crystal ($E_{\text{em}}=2.95$ eV, i.e., 419.6 nm) observed under the same excitation. The similarity of the spectra points to the fact that the thermal treatment results in the production in the CsCl:Pb crystal of CsPbCl₃ nanocrystals dispersed in a CsCl matrix.

As the excitation energy increases up to 7.3 eV (170 nm), besides the above-mentioned narrow 2.98 eV band, a broader complex band peaking at 3.94 eV (315 nm) is observed in the emission spectrum of the annealed CsCl:Pb crystal. Unlike a single crystal of CsPbCl₃ where only the fast 2.95 eV luminescence has been observed, the fast and the slow components can be detected in the decay kinetics of the 2.98 eV emission of the annealed CsCl:Pb crystal under excitation in some energy regions. The reason of the appearance of the additional decay components will be explained later.

The maxima of the excitation spectrum measured for the fast component of the CsPbCl₃ nanocrystals emission (indicated by arrows) coincide with the corresponding minima in the excitation spectrum of the free exciton luminescence of a CsPbCl₃ single crystal (Fig. 1, curves 1 and 3). It means that the excitation spectrum of the emission of CsPbCl₃ nanocrystals coincides with their absorption spectrum and that, unlike in the case of a CsPbCl₃ single crystal, this excitation spectrum is not distorted by the absorption at the nanocrystal surface. This effect is caused by a small size of the CsPbCl₃ nanocrystals. The excitation efficiency of the fast component of the CsPbCl₃ nanocrystals emission decreases noticeably at $E_{\text{exc}} > 6.8$ eV (Fig. 1, curve 1). It may be explained by a more effective excitation of the Pb²⁺ centres emission in this energy region (see curves 4 and 5). The appearance of the slow component in the decay kinetics of the 2.98 eV emission of CsPbCl₃ nanocrystals is a result of the reabsorption by the CsPbCl₃ nanocrystals of the 3.94 eV emission of the Pb²⁺ centres where the slow component is the dominating one (Fig. 1, curve 2 and 4, 5).

In the band-to-band transitions region of a CsCl crystal (from 8.3 to 14 eV), the direct optical excitation of CsPbCl₃ nanocrystals as well as their indirect excitation (e.g., due to their recombination with electron-hole pairs) does not practically occur.
Under excitation by photons of $E_{\text{exc}} > 14$ eV energy, a fast core-valence luminescence of CsCl is observed. This luminescence is effectively reabsorbed by CsPbCl$_3$ nanocrystals due to the coincidence of its spectrum with the absorption spectrum of CsPbCl$_3$. This channel of the fast CsPbCl$_3$ luminescence excitation in the annealed CsCl:Pb crystal explains the presence of the fast X-ray luminescence of CsPbCl$_3$ microcrystals dispersed in a CsCl matrix [2].

The decay curve of the CsPbCl$_3$ nanocrystals luminescence obtained under excitation in the transparency region of a CsCl:Pb crystal can be approximated by two exponents with decay times $\tau_1 = 0.15$ ns and $\tau_2 = 12.1$ ns. For the 2.95 eV emission of a CsPbCl$_3$ single crystal, the corresponding values are $\tau_1 = 0.48$ ns and $\tau_2 = 7$ ns. The smaller value of $\tau_1$ obtained for CsPbCl$_3$ nanocrystals as compared with that characteristic of a CsPbCl$_3$ single crystal is explained as an evidence of the quantum size effect (see also [1]). Under excitation in the 6.0 eV to 7.8 eV energy range, the decay kinetics of the CsPbCl$_3$ nanocrystals emission coincides with that of the triplet 3.94 eV emission of Pb$^{2+}$ vacancy centres. The observed decay kinetics of the CsPbCl$_3$ emission points to the reabsorption of the Pb$^{2+}$ vacancy emission by the CsPbCl$_3$ nanocrystals.

Under excitation by photons of $E_{\text{exc}} > 14$ eV energy, the initial part of the luminescence decay curve of the CsPbCl$_3$ nanocrystals studied can be described as consisting of two exponents with decay times $\tau_1 = 1.3$ ns and $\tau_2 = 18.6$ ns. The presence of decay component with $\tau = 1.3$ ns is a result of the reabsorption by CsPbCl$_3$ nanocrystals of the CsCl core-valence luminescence which has decay time about 1.3 ns and can be excited only at $E_{\text{exc}} > 14$ eV.

Thus, the presence of the slow decay component in the luminescence of CsPbCl$_3$ nanocrystals thermally created in a CsCl:Pb crystal as well as the small efficiency of energy transfer from the CsCl matrix to CsPbCl$_3$ nanocrystals may limit possible applications of this system.

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![Graph](image_url)

Fig. 1. Excitation spectra: (a) of the fast (curve 1) and slow (curve 2) decay components of the 2.98 eV emission of CsPbCl$_3$ nanocrystals; (b) of the free exciton 2.95 eV emission of a CsPbCl$_3$ single crystal (curve 3), and of the fast (curve 4) and slow (curve 5) decay components of the (3.94 eV) emission of Pb$^{2+}$ vacancy centres in CsCl:Pb. T=10 K.

References
